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(54) CORROSION-RESISTANT METAL COATINGS

(71) We, PYRENE CHEMICAL SERVICES LIMITED, a British Company, of Ridgeway, Iver, Buckinghamshire SL0 9JJ, do hereby declare the invention, for which we pray

that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion-resistant coatings, based on aluminium phosphate, for metal surfaces. It is an object of this invention to provide a process for forming a coating on a metal, the coating having good corrosion resistance and providing a good undercoat for painting.

It is well known to use coatings based on phosphates and chromates to provide anti-corrosive coatings or undercoats for painting. The coatings based on phosphates may be divided into those based on crystalline phosphates and those based on non-crystalline iron phosphates.

All these coatings show some disadvantages, however. For example, although a coating based on manganese phosphate gives good corrosion resistance, it is not suitable as an undercoat for painting articles which may undergo intense plastic deformation. Conversely, a thin coating based on non-crystalline iron phosphate gives good plastic deformation properties, but shows poor corrosion resistance. A coating based on chromates has generally excellent corrosion-resistant properties but may show, over the course of time, undesirable results when used as an undercoat for painting. The use of hexavalent chromium ion is unsuitable because of the consequent environmental pollution.

It is also known to use compositions comprising aluminium and phosphate ions for the provision of electrically insulating coatings on metals. However, as is well known in the art, these coatings have to be much thicker than corrosion-resistant coatings, and the problems associated with the two types

of coatings are known to be largely independent of each other.

It has been proposed to include a minor amount of aluminium ions in a phosphating solution in order to inhibit the etching of the metal being coated in the formation of a coating based on zinc phosphate, and also to reduce the weight of coating. Japanese Patent Kokai No. 8511/74 discloses a system in which aluminium ions, e.g. as aluminium phosphate, are included in a phosphating solution having a pH ranging from 3.5 to 5. A coating containing iron phosphate as the principal ingredient and minor amounts of aluminium phosphate and iron oxides in order to enhance the corrosion resistance of the chemical conversion coating is achieved. However, we have now found that the plastic deformation and corrosion resistance properties of the coating may be still further improved.

According to the invention, a corrosion-resistant coating consisting substantially of aluminium phosphate is formed on a metal surface by a process comprising applying to the surface an aqueous acidic composition having a pH of from 1.5 to 3.5 and comprising phosphate ions and aluminium ions, the aluminium ions being present in an amount of from 0.01 to 10 grams per litre of the composition.

The aluminium ions may be included in the composition in the form of an aluminium compound such as aluminium nitrate, aluminium hydroxide or aluminium sulphate. The compound may be added either in solid form or as a solution into the acidic phosphating bath. The pH of the bath may then be adjusted as necessary. The content of aluminium ion in the bath is preferably in the range of from 0.2 to 3 grams/litre. If the amount is less than 0.01 grams/litre, then too thin a coating will result, whereas too high a content of aluminium ions is unfavourable economically.

The acidic phosphating solution preferably contains from 1 to 100 grams/litre,

most preferably from 5 to 50 grams/litre of phosphate ions. The source of phosphate ions may be, for example, phosphoric acid, sodium dihydrogen phosphate or disodium hydrogen phosphate, in aqueous solution. For example, dilute phosphoric acid may be added with an aluminium compound, the pH of the composition then being adjusted to a value of from 1.5 to 3.5 by adding alkali e.g. caustic soda, caustic potash or ammonia solution.

It is found that if the pH of the composition is less than 1.5, the etching action on the metal surface being treated is significant, whereas at a pH of more than 3.5, aluminium phosphate and aluminium hydroxide are precipitated.

If desired, the acidic phosphating solution may contain an oxidising agent and a promoter for forming the coating. Suitable additives are nitrate and/or chlorate ions in concentrations of up to 20 grams/litre, preferably of from 1 to 5 grams/litre, and/or nickel ions in a concentration of up to 5 grams/litre, preferably of from 0.01 to 2 grams/litre. The solution may also contain sulphate ions in a concentration of up to 10 grams/litre in order to increase the film weight.

Particularly suitable metals for coating by the process of the invention include iron, steel, zinc or zinc-galvanised steel, aluminium and aluminium alloys.

The process of the invention may be carried out by immersing the metal surface to be coated in, or spraying it with, the phosphating solution at 30 to 90°C for 1 to 5 minutes to form a chemical conversion coating in conventional manner. Alternatively the metal may be subjected to electrolytic conversion with alternating current by employing the metal as one electrode and, for example, the metal itself, carbon, aluminium or stainless steel as the other electrode. The distance between the two electrodes may be from 2 to 50 cm at a current density, measured in Amps per square decimeter, of from 0.1 to 20 A/dm square, preferably from 3 to 5 A/dm square, for from 5 seconds to 5 minutes. The coating may also be applied by direct current if, of the two electrodes mentioned above, the metal to be phosphated is the cathode. If necessary, the electrolytic conversion may be combined with the chemical conversion by dipping.

A colourless or bluish interference coating is formed on zinc or zinc-galvanised steel, and a bluish-green or violet interference coloured coating is formed on steel surfaces, by the above chemical or electrolytic conversion processes.

It has been confirmed by chemical analysis that the composition of the resultant coating consists of aluminium phosphate

($\text{AlPO}_4 \cdot x\text{H}_2\text{O}$). Iron ions have been detected in minor amounts.

The weight of coating formed generally ranges from 0.2 to 1.5 g/m². Microscopic observation shows that the coating is very thin and has a non-crystalline appearance. Despite this fact, when subjected to the saline-spraying test according to JIS-Z-2371, it is shown to have excellent anti-corrosion properties in comparison with conventional phosphating coatings such as those based on iron phosphate, with zinc phosphate coatings having a coating weight ranging from 1 to 3 grams/m² used conventionally as undercoats for painting, and with colourless chromate coatings having similar appearance to those based on iron phosphates and used as temporary anti-corrosive coatings.

The coatings produced by the process of the invention show similar or better performances than the above comparative coatings in the adhesion of paint, and corrosion resistance after painting.

The following are some examples of the invention.

EXAMPLE 1

Process: Chemical conversion by dipping for 3 minutes at 60°C.

Specimens: SPCI steel plate (70×150×0.8 mm).

Composition of phosphating solution:

	grams	
75% Phosphoric acid ...	31.4	100
Aluminium hydroxide ...	2.3	
98% Sulphuric acid ...	1.0	
Sodium nitrate ...	4.3	

The concentrate was made up to 1 litre by diluting it with water and the pH of the diluted solution was adjusted to 2.4 with caustic soda.

The phosphating treatment under these conditions formed a non-crystalline coating of 1 g/m² having an interference colour. When the specimen was subjected to the saline spraying test, no stain could be observed even after 90 minutes. When the saline spraying test was carried out on specimens applied with commercially available phosphating solution based on iron or zinc phosphates, stains could be observed after 30 minutes.

When the same specimen, treated under the conditions of Example 1 but with the pH adjusted to 5, was subjected to the saline spraying test, stain could be observed after 15 to 30 minutes. It appeared that, due to the high pH value of the solution, the conversion coating contained less aluminium phosphate and more iron phosphate.

EXAMPLE 2

Process: Alternating current electrolytic conversion at 65°C.

Specimen: Zinc galvanised steel plate (70×150×0.27 mm).
Composition of 1 litre of phosphating solution (adjusted to pH 2.5):

75% Phosphoric acid	grams
Aluminium hydroxide	45.7
Aluminium nitrate	2.6
Water	6.3
	balance

Alternating current electrolytic conditions:

Current density: 5 A/dm²
Current duration: 20 seconds
Ratio of electrodes: 1:1
Distance between electrodes: 50 mm
Electrodes: Specimen and carbon plate.

After treatment, the specimen was found to have a non-crystalline coating having an interference or greyish white colour.

The specimen was then subjected to the saline spraying test, and no stain could be observed for 24 hours. On the other hand, when the specimen was treated with a commercially available phosphating solution based on zinc phosphate, stains of white rust were evident after 3 hours.

The specimen, as treated in Example 2, was then painted with an acrylic-paint. The saline spraying test on the painted specimen did not give rise to any change in appearance even after 150 hours or more, neither was any change observed on the adhesion of the paint after subjection to the Erichsen test on a scratched specimen (after pressing by an Erichsen film tester, followed by a friction pull test with Scotch tape).

EXAMPLE 3

Process: Cathodic electrolysis conversion at 70°C

Specimen: SPCT steel plate (70×150×0.8 mm)

Composition of 1 litre of phosphating solution (adjusted to pH 2.55 with NaOH):

75% Phosphoric acid	grams
Aluminium nitrate	39.2
Sodium chlorate	11.3
Water	1.1
	balance

Direct current electrolytic conditions:

Current density: 5 A/dm²
Current duration: 30 seconds
Electrodes: Specimen and carbon plate
Ratio of cathode area to anode area: 1:1
Distance between electrodes: 40 mm

After the treatment, a non-crystalline coating with an interference colour was obtained on the specimen. When the specimen was subjected to the saline spraying test, no stain could be observed after 1 hour.

WHAT WE CLAIM IS:—

1. A process in which a corrosion-resistant coating consisting substantially of aluminium phosphate is formed on a metal surface, the process comprising applying to the surface an aqueous acidic composition which has a pH of from 1.5 to 3.5 and which comprises phosphate ions and from 0.1 to 10 g/l of aluminium ions.
2. A process according to claim 1 in which the composition comprises from 0.2 to 3 g/l of aluminium ions.
3. A process according to claim 1 or claim 2 in which the composition comprises from 1 to 100 g/l of phosphate ions.
4. A process according to claim 3 in which the composition comprises from 5 to 50 g/l of phosphate ions.
5. A process according to any preceding claim in which the composition additionally comprises up to 20 g/l of nitrate ions and/or up to 20 g/l of chlorate ions.
6. A process according to any preceding claim in which the composition additionally comprises up to 5 g/l of nickel ions.
7. A process according to any preceding claim in which the composition additionally comprises up to 10 g/l of sulphate ions.
8. A process according to any preceding claim in which the metal which is coated is of iron, steel, zinc, zinc-galvanised steel, aluminium or aluminium alloy.
9. A process according to any preceding claim in which the metal surface is immersed in, or sprayed with, the aqueous acidic composition.
10. A process according to any of claims 1 to 8 in which the coating is formed electrolytically on the metal surface.
11. A process according to claim 1 substantially as herein described with reference to any of the Examples.
12. A metal surface having thereon a corrosion-resistant coating consisting essentially of aluminium phosphate which has been formed by a process according to any preceding claim.

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